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Symmetry-restricted local-density-functional calculation are reviewed and the resultant curve-crossings analyzed for the case of Al_4 in its singlet manifold at electronic states. Curve-crossing are avoided using an extension of the functional occupation number method.

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Introduction

The $X\alpha$ method¹ and its offspring are becoming more and more important in quantum chemistry for chemical systems that are too large for accurate configuration interaction (CI) calculations. All self-consistent-field (SCF) methods of quantum chemistry method begin with one or more systems of one-electron equations of the form,

$$\epsilon_i \phi_i(\mathbf{r}) = \left[-\frac{1}{2} \nabla^2 + V \right] \phi_i(\mathbf{r}). \quad (1)$$

Invariably V is separated into its one-electron and two-electron parts, the electron-nuclear interaction potential, V_{en} , and the electron-electron interaction potential, V_{ee} , respectively. Only V_{ee} distinguishes the various SCF methods of quantum chemistry. In what are now called local density functional (LDF) methods the electron-electron potential is written,

$$V_{ee} = V_{ee}(\mathbf{r}_1) = \int \frac{\rho(\mathbf{r}_2) d\mathbf{r}_2}{r_{12}} + V_{xc}(\rho(\mathbf{r}_1)), \quad (2)$$

where the total electron density, ρ , can be divided into spin-up and spin-down components, and the expression for the spin-up component,

$$\rho_{\uparrow}(\mathbf{r}) = \sum_i n_i \phi_{i\uparrow}^*(\mathbf{r}) \phi_{i\uparrow}(\mathbf{r}), \quad (3)$$

where the n_i are the (possibly fractional) number of electrons occupying each orbital of Eq. 1, contains an implicit summation over orbital index i . These methods are called LDF's because the exchange and correlation potential, $V_{xc}(\rho(\mathbf{r}_1))$, at any point in space is constrained to depend only on the density at the same point. If we constrain V_{xc} to be local and require the system of equations to satisfy the virial theorem at all extrema on all Born-Oppenheimer potential energy surfaces, we are led to the $X\alpha$ approximation for spin-up orbitals,

$$V_{xc}^1(\rho(\mathbf{r}_1)) = 3\alpha \left(\frac{3}{4\pi} \rho_{\uparrow}(\mathbf{r}) \right)^{1/3}. \quad (4)$$

This result follows from simply considering the homogeneous electron gas at all densities and requires that LDF expressions not include gradients of the density. The value of α for the homogeneous electron gas based on variation is two-thirds² and based on averaging is one.¹ For heteronuclear molecules the best choice is perhaps 0.7.

On the other hand, the Kohn-Sham² mapping of the the ground state of the real system onto the ground state of a fictitious noninteracting set of electrons, which has the same density as the real system, provides a different interpretation of these equations. If both the real and noninteracting sets of electrons are nondegenerate, the mapping is one-to-one and the wavefunction of the noninteracting set of electrons is a single determinant of one-electron orbitals likely satisfying Eq. 1 for some V . (The counterexamples of non- V -representability use degeneracy of one-electron orbitals.³⁻⁵) If we map the energy of a single-determinant of plane-wave orbitals onto the essentially exact energy⁶ of the homogeneous electron gas as a function of background positive charge density in the completely spin-paired and completely spin-polarized extremes, we are led to a different set of LDF's that typically overbind molecules compared to $X\alpha$ and experiment.⁷ The best of this other set is perhaps the Perdew-Zunger (PZ) parameterization,⁸ which, although it is too complicated to write out here, gives, apart from slightly rescaling the total energies, the same description of most nonmagnetic molecules as does $X\alpha$. The reason for almost no difference is that the one-third power and functions similar to it tremendously deamplify variations in the nonnegative density itself.

The computational attraction of Eq. 1 and 2 is that $V(\mathbf{r})$ is a local potential, i.e., it is the same for each orbital.⁹ While all the orbital generating equations of quantum chemistry can be rendered in the form of Eq. 1 (if all else fails by using projection) only with a local potential is $V(\mathbf{r})$ a single-valued (orbital independent) function of position. Thus obtaining $V(\mathbf{r})$ is central to all local potential methods and that problem is straightforward. Eqs. 1-3 can be solved for any real vector of occupation numbers, \mathbf{n} . All LDF approximations to V_{xc} yield local potentials, but not all local potentials result from LDF approximations, as is obvious from the direct Coulomb term in Eq. 2.

For any density functional expression for V_{xc} the coupled one-electron equations of motion, Eq. 1, can be integrated to yield the total energy expression,

$$E = \langle T \rangle + \langle U \rangle, \quad (5)$$

where the total kinetic energy is given by an expression,

$$\langle T \rangle = -\frac{1}{2} n_i \phi_{i,s}^*(\mathbf{r}) \nabla^2 \phi_{i,s}(\mathbf{r}), \quad (6)$$

containing an implicit summation over the two spin directions through the index s , and

$$\langle U \rangle = \int \rho_s(\mathbf{r}) U_s(\rho(\mathbf{r})) d\mathbf{r}, \quad (7)$$

where the one-electron potential and the density functional potential energy operator, U , are related by an independent variation of $\langle U \rangle$ with respect to each spin density at each point,

$$\int V_1(\rho) \delta \rho_1(\mathbf{r}) d\mathbf{r} = \delta \langle U \rangle \quad (8)$$

For any part of V that is approximated as being an LDF, Eq. 8 is precisely a differentiation,

$$V_1^{LDF}(\mathbf{r}) = \frac{d [\rho_s(\mathbf{r}) U_s^{LDF}(\rho(\mathbf{r}))]}{d \rho_1(\mathbf{r})}. \quad (9)$$

That Eq. 8 does not hold for a nonLDF contribution to V is obvious if one considers multiplying Eq. 2 by $\rho(\mathbf{r}_1)$. In that case the $\rho(\mathbf{r}_1)$ and $\rho(\mathbf{r}_2)$ in the direct Coulomb term are asymmetrical; \mathbf{r}_2 is an integration variable while \mathbf{r}_1 is not.

As is the case with Hartree-Fock-based quantum chemical methods, the analytic basis set approach is the overwhelming favorite in nonmuffin-tin local potential quantum chemical methods, except for lower dimensional problems such as atoms¹⁰ and linear molecules.¹¹⁻¹³ The all-purpose analytic basis set is Gaussians^{7,14} in both quantum chemical methods. In contrast to Hartree-Fock based methods, computational efficiency dictates and complicated expressions such as Eq. 4 inspire fitting V in analytic-basis-set local potential methods.¹⁵⁻¹⁶ If the potential is fit, which is indicated by placing a bar over the fitted quantity, then the potential energy should be evaluated,¹⁷

$$\langle U \rangle \approx \int \rho(\mathbf{r}) \overline{V}(\rho(\mathbf{r})) d\mathbf{r} + \int \overline{\rho(\mathbf{r}) [U(\rho(\mathbf{r})) - V(\rho(\mathbf{r}))]} d\mathbf{r}, \quad (10)$$

because then the nonfitted density only occurs multiplied by the local potential. Variation with respect to the orbitals (occurring only in the nonfitted density) gives the local potential term of the one-electron equations, and the total energy is insensitive in first order to changes of the one-electron

orbitals, provided the fitting procedure follows variationally from this equation. Eq. 10 yields an energy-stationary way to fit the charge density,^{7,18} to fit the direct electron-electron Coulomb potential itself,¹⁹ and to fit the $X\alpha$ exchange potential.^{7,20} For the more complicated V_{xc} such as occur in the PZ functional, Eq. 10 yields variational weights for any numerical fitting scheme.²¹

Independent of how V is determined, it is natural to ask what symmetry it has and to what extent symmetry can help in local potential calculations. The system of equations is nonlinear, and therefore its solutions can and do yield densities that break the symmetry of the collection of nuclear charges.²² There are three approaches to this important problem. First, one can accept broken-symmetry solutions.²³⁻²⁶ Second, one can restrict one's attention to density functional methods that yield V having the symmetry of the nuclear charges.³⁻⁵ Third, one can explicitly symmetrize V by symmetrizing a broken-symmetry wavefunction before computing the kinetic energy and density during the SCF process.²⁷

Empirically, the experimental ionization potential of a core-hole from a set of symmetry-equivalent atoms is better reproduced in local potential methods when symmetry is broken and the hole self-consistently localizes on one of that set of atoms.^{23,24} Unfortunately, in contrast to *ab initio* methods, the variational principle does not also suggest this solution. In current local potential methods, a localized core hole results in a higher total energy than a delocalized-hole total energy. When applied to spin, symmetry-restriction leads to a poor description of Cr_2 ,^{25,26} which has a singlet electronic ground state but must dissociate into two septet atoms. All current LDF methods, however, are not invariant under rotations in spin space.^{22,28} Therefore they can never yield spin-densities that transform properly for any magnetic system that has any minority-spin electrons, without further assumptions (such as using the same orbitals for the two spins). Nevertheless, significant progress is being made in interpreting solutions in which the density is invariant but the spin densities break the molecular symmetry^{29,30} (spin density waves). Apart from the special case of core holes, there has been no general attempt to interpret broken-spatial-symmetry solutions (charge density waves) despite the fact that they often arise asymptotically in molecular dissociation.^{11,31} In cases where the real system does not exhibit charge-density-wave behavior, these broken-spatial-symmetry errors typically make binding energies uncertain at the tenth of an electron volt level.

Symmetrizing V removes this uncertainty. (For atoms this means making the central field approximation.) Furthermore, a symmetrized V can be readily taken advantage of in linear-combination-of-atomic-orbitals

(LCAO) local potential computer codes.²² Symmetrization without further approximation allows routine LDF calculations on symmetric systems containing tens of transition metal atoms,³²⁻³⁴ or larger mixed system such as C₆₀ and yttrium diphtalocyanine (YC₆₄H₃₂N₁₆).^{35,36}

In what follows a density functional theory^{27,28} of the broken-spatial-symmetry problem for singlet electronic states is reviewed. It relies on the fact the density is to be symmetrized, which, in turn, symmetrizes V provided it is a function of the density. This symmetrization validates the fractional occupation number (FON) description of the ground state.³⁷ The theory contains the mathematics of *ab initio* configuration interaction. A good introduction to any discussion of correlation and LDF theory is the work of Cook and Karplus.³⁸

FON Singlet-State Configuration Interaction

The simplest densities to consider correspond to closed-shell molecules, in which the density clearly has the symmetry of the molecule. For such a molecule consider the case where the highest occupied molecular orbital (HOMO) is antibonding and the lowest-unoccupied molecular orbital (LUMO) is bonding and compress the appropriate internuclear separations until these orbitals become nearly degenerate (or consider the opposite case and expand the bonds). For concreteness, consider a $^1\Sigma_g^+$ state of a homonuclear diatomic molecule and a broken-symmetry HOMO of mixed σ_g and σ_u character,

$$\phi = a\chi_{\sigma_g} + b\chi_{\sigma_u}. \quad (11)$$

The g and u components must be orthogonal from symmetry considerations alone. (If they are also normalized, then the sum of the magnitudes squared of a and b is unity.) Since the kinetic energy operator is invariant under any spatial symmetry operation, ϕ 's contribution to the kinetic energy,

$$T_\phi = -a^*a \langle \chi_{\sigma_g} | \frac{1}{2} \nabla^2 | \chi_{\sigma_g} \rangle - b^*b \langle \chi_{\sigma_u} | \frac{1}{2} \nabla^2 | \chi_{\sigma_u} \rangle, \quad (12)$$

is diagonal in its components; thus the kinetic energy is the same as that of a symmetry-restricted FON calculation using $n_{\sigma_g} = a^*a$ and $n_{\sigma_u} = b^*b$. In contrast to the situation for the overlap and kinetic energy, there is a difference between the broken-symmetry and symmetry-restricted densities. The difference is the unsymmetrical expression,

$$a^*b u_{\sigma_g}^* u_{\sigma_u} + b^*a u_{\sigma_u}^* u_{\sigma_g}, \quad (13)$$

that has larger magnitude on either the left-hand atom or on the right hand atom depending on the magnitudes and phases of a and b . If, however, the density is symmetrized by, in this case, averaging the original

broken-symmetry orbital density with the same density after inverting the coordinate system, then both orbital densities are the same,

$$a^* a u_{\sigma_g}^* u_{\sigma_g} + b^* b u_{\sigma_u}^* u_{\sigma_u}. \quad (14)$$

Thus symmetrized-broken-symmetry and the FON density-functional calculations are identical. For the above example, both give a charge density consistent with a $^1\Sigma_g^+$ electronic state.

FON SCF calculations are always slower to converge than fixed-occupation-number LDF calculations. This is precisely because there is at least one more degree of freedom involved. Another way to analyze this slowness is to note that for fixed occupation-number calculations, the relevant gauge of speed of convergence is the gap between the HOMO and LUMO energies,³⁹ whereas FON convergence is also strongly influenced by the density of states surrounding the HOMO and LUMO energies.¹⁷ (For the FON case, the HOMO must be defined as the highest level that is greater than half occupied and the LUMO is the lowest level that is less than half occupied.) Therefore it is best to avoid direct FON calculations if one can.

To an excellent approximation the total LDF energy is a quadratic function of the occupation numbers,³⁷ because all of its components except V_{xc} are, and V_{xc} is a very slowly varying function of the density. This quadratic property is also suggested by the fact that the exact total energy depends only on the first and second order density matrices. If the LDF energy is a quadratic function of the occupation numbers, then the LDF one-electron eigenvalues, which are the derivatives of the total energy with respect to the corresponding occupation number,⁴⁰

$$\epsilon_{i,s} = \frac{\partial E}{\partial n_{i,s}} \quad (15)$$

must be linear functions of the occupation numbers. In particular, this approximation means that for the σ_g and σ_u orbitals under consideration,

$$\Delta\epsilon = \epsilon_u - \epsilon_g \quad (16)$$

varies linearly with fractional number of electrons, n , transferred from the σ_g orbital to the σ_u orbital. The value of this eigenvalue difference for all numbers of electrons transferred then follows from the lagrange interpolating formula,

$$\Delta\epsilon(n) = \Delta\epsilon(0) \frac{(n-2)}{(0-2)} - \Delta\epsilon(2) \frac{(n-0)}{(2-0)}, \quad (17)$$

which reduces,

$$\Delta\epsilon(n) = \Delta\epsilon(0) - [(\Delta\epsilon(2) - \Delta\epsilon(0))\frac{n}{2}]. \quad (18)$$

There is an FON solution $\Delta\epsilon(n_f) = 0$, if and only if

$$\Delta\epsilon(0) \Delta\epsilon(2) < 0. \quad (19)$$

In that case, transferring n_f electrons,

$$n_f = \frac{2\Delta\epsilon(0)}{\Delta\epsilon(0) - \Delta\epsilon(2)}. \quad (20)$$

gives the FON ground state.

Integrating to get the total energy at the FON solution from the $n = 0$ limit,

$$\Delta E = \int_0^{n_f} \Delta\epsilon(n) dn \quad (21)$$

gives one formula for the FON total energy,

$$E_{f0} = E(0) + \frac{\Delta\epsilon(0)^2}{\Delta\epsilon(0) - \Delta\epsilon(2)}, \quad (22)$$

and integrating from the other limit gives another formula,

$$E_{f2} = E(2) + \frac{\Delta\epsilon(2)^2}{\Delta\epsilon(0) - \Delta\epsilon(2)}. \quad (23)$$

Lagrange interpolating between these two expressions for the FON total energy gives an FON energy,²⁸

$$E_l = \frac{-E(0)\Delta\epsilon(2) + E(2)\Delta\epsilon(0) - \Delta\epsilon(0)\Delta\epsilon(2)}{\Delta\epsilon(0) - \Delta\epsilon(2)}, \quad (24)$$

that connects continuously to the pure state solutions outside the FON range, geometries for which Eq. 19 is not satisfied.

The FON energy lowering can be viewed as resulting from configuration interaction between the $n = 0$ and the $n = 2$ states, in which the upper FON energy,

$$E_u = \frac{E(0)\Delta\epsilon(0) - E(2)\Delta\epsilon(2) + \Delta\epsilon(0)\Delta\epsilon(2)}{\Delta\epsilon(0) - \Delta\epsilon(2)}, \quad (25)$$

lies as much higher in energy above the average of $E(0)$ and $E(2)$ as E_l lies below that average. This approach can be extended to the general

$n \times n$ configuration interaction problem. In such an extension the pure state energies become diagonal entries in an $n \times n$ eigenvalue problem. In this eigenvalue problem one adds an off-diagonal matrix between any two pure states,

$$V = \frac{\sqrt{(E_l - E_u)^2 - (E(0) - E(2))^2}}{2} \quad (26)$$

if and only if the two pure states differ precisely in that two electrons are transferred from one orbital to another and that the eigenvalue difference between these two orbitals change according to Eq. 19 in going from the one state to the other. This postulate gives as its ground state the FON solution when restricted to only allowing a single pair, but any single pair, of states to exchange electrons.

Al₄

The X α ground state of Al₄ is a D_{2h}-symmetric rhombus with triplet electronic configuration having a spin-up electron in each of the $9a_{1g}$ and $1b_{1u}$ orbitals outside a 50-electron $8a_g^2 2b_{1g}^2 3b_{1u}^2 1b_{2g}^2 5b_{2u}^2 1b_{3g}^2 5b_{3u}^2$ closed-shell configuration. The b_{1g} orbital is a π orbital with nodal plane in the plane of the molecule. This agrees with an *ab initio* description.⁴¹ The triplet-state atomization energy (the energy required to dissociate the molecule into four separated R(3)-symmetrized spin-polarized atoms) is 6.52 eV, its bond distance is 4.99 bohr, and it has a bond angle of 88°.

Much more interesting than the ground state potential energy surface are the singlet potential energy surfaces. Fig. 1a gives the symmetry-restricted low-lying surfaces in square-planar D_{4h} symmetry. These breathing-mode surfaces are derived from the 54-electron $5a_{1g}^2 1a_{2g}^2 2a_{2u}^2 4b_{1g}^2 2b_{2g}^2 1b_{2u}^2 1e_g^4 5e_u^4$ configuration by annihilating two electrons from the valence a_{1g} , a_{2u} , b_{1g} , and b_{2g} orbitals respectively. There are five curve crossings in the figure. This case is ideal for using Eqs. 24-26 in a 4×4 eigenvalue problem. The result is the solid lines of Fig. 1b, where all crossings, of the original, dashed lines, are avoided.

The most interesting avoided crossing in Fig. 1b is the one, at smallest Al-Al bond distance, between the a_{1g}^0 and b_{1g}^0 states. It is the weakest. This is because the a_{1g} orbital, being nodeless, is largely centered on the atomic centers, like the b_{1g} orbital which, being $d_{x^2-y^2}$ -like, has nodes at the bond centers for atoms chosen as they were to lie in the $\pm x$ and $\pm y$ directions. Because the densities are similar, transferring two electrons between these two orbitals has the smallest effect on their eigenvalue difference, and the configurations do not repel each other very much.

This is not the whole story for singlet Al₄, by any means. Fig. 2a considers D_{2h}-symmetric bending motion at the minimum Al-Al bond distance

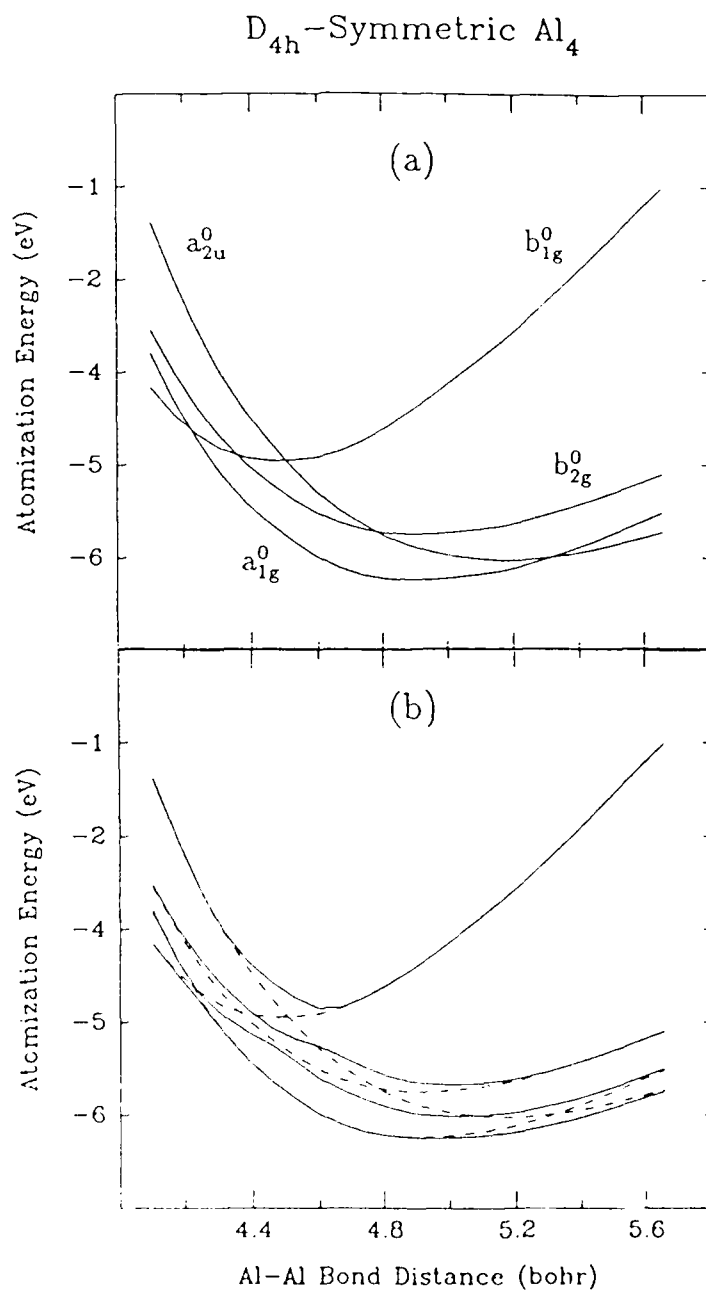


Figure 1. Breathing mode potential energy curves for singlet square-planar Al_4 .

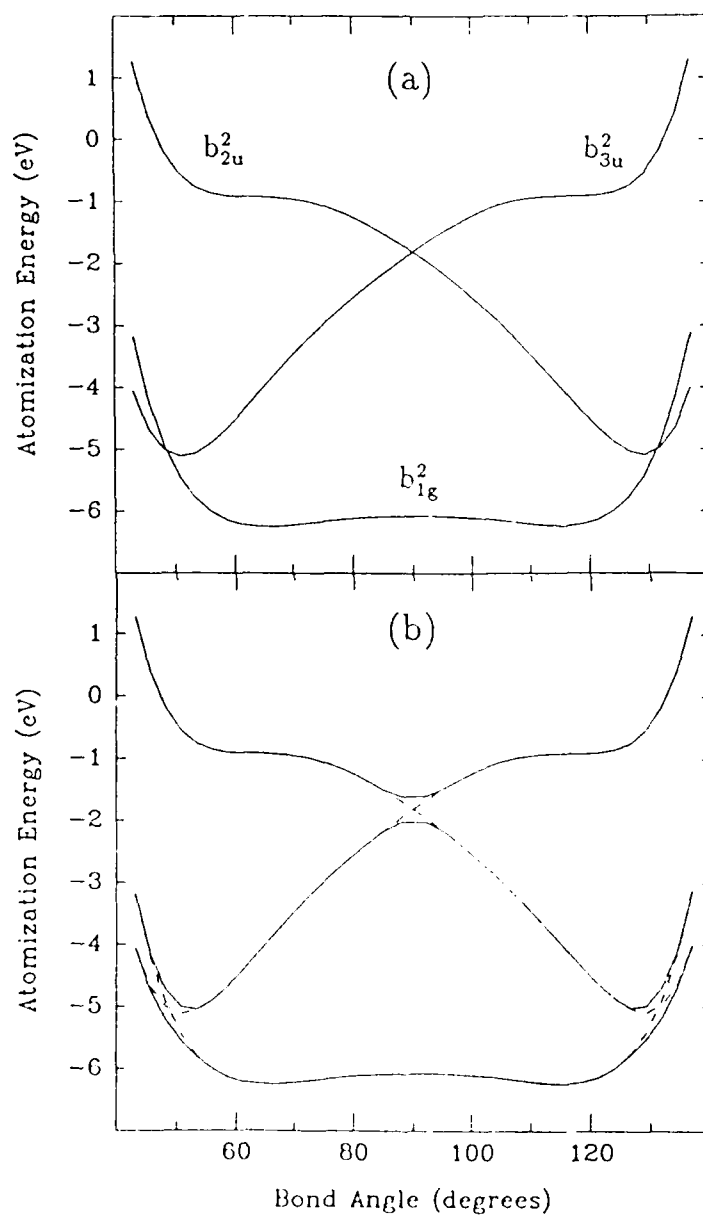
D_{2h} -Symmetric Al_4 

Figure 2. In-plane bending potential energy curves for singlet Al_4 for Al-Al bond distances of 4.9 bohr.

of 4.9 bohr in Fig. 1, where the ground state is largely a_{1g}^0 . Under this motion, the a_{1g}^0 state interacts with two p -like states that have nodes along the shortest Al-Al second neighbor bond when they cross the a_{1g}^0 state. These two p -like states are degenerate in D_{4h} symmetry and thus are different, higher lying in energy, from the states considered in Fig. 1. Fig. 2b gives the result of using Eqs. 24-26 on the pure states of Fig. 2a.

Conclusions

The work of defining local potential, $X\alpha$ -like, methods for use in quantum chemistry is not done. Only pure singlet states were addressed in this work, and only methods that resulted in no net spin-polarization anywhere in space were used. The problem of coupling spin, fractional occupation numbers, and symmetry in a complete approximate LDF theory^{22,27,28} is unfinished.

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